

MELTLESS PREPARATION OF MARTENSITIC STEEL ARTICLES
HAVING THERMOPHYSICALLY MELT INCOMPATIBLE
ALLOYING ELEMENTS

[0001] This invention relates to the preparation of metallic-alloy articles, specifically martensitic iron-base alloy articles, without melting of the metallic alloy.

BACKGROUND OF THE INVENTION

[0002] Martensitic steels having a martensitic microstructure are one important class of the ferritic steels. The martensitic steels have wide application in the aircraft propulsion industry and are also used in other industries such as the automotive industry. Metallic articles made of martensitic steels are fabricated by any of a number of techniques, as may be appropriate for the nature of the metal and the article. In one common approach, metal-containing ores are refined to produce molten metal, which is thereafter cast. Ore refinement may take place separately for each of the major alloying elements, or in combination for more than one element. Elements and combinations of elements may take many intermediate forms before being melted to form the final alloy. The metal is refined as necessary to remove or reduce the amounts of undesirable minor elements. The composition of the refined metal may also be modified by the addition of desirable alloying elements. These refining and alloying steps may be performed during the initial melting process or during remelting. After a desired martensitic composition is produced, it may be used in the as-cast form for some compositions (i.e. cast martensitic steels), or it may be cast and further worked to form the metal to the desired shape for other compositions (i.e. wrought martensitic steels). It may instead be atomized to form fine powder and subsequently consolidated and, in some cases, further worked (i.e. powder metallurgy martensitic steels). In any case, further processing such as heat treating, machining, surface coating, and the like may be employed.

[0003] Regardless of the processing route, all of these forms involve melt processing and are, as a result, subject to restrictions imposed by such processes. The melting of martensitic-composition steels is typically accomplished using multiple melt processes for premium-quality material in order to refine undesirable residual element content, to homogenize the overall composition, and to adjust the alloy content; or by single-melt processes and subsequent ladle modifications for standard-quality material. In either case, the melt is cast to produce the final ingot or article. In multiple melt processes, intermediate cast electrodes are produced which serve as the input stock to the subsequent melting step. Melting processes include those which are not performed under vacuum such as electroslag remelting, air melting, basic-oxygen-furnace melting, open-hearth-furnace melting, and electric-arc-furnace melting followed by argon-oxygen decarburization, and those which are performed under vacuum such as vacuum induction melting, vacuum arc remelting, and vacuum oxygen decarburization. Non-vacuum processes require the use of refining and protecting slags during the melting process. In any case, additional chemistry modifications may take place in the ladle to refine impurity content and to add additional alloying elements.

[0004] Additional limitations are also imposed as a result of the melting process for martensitic steels because of their composition. Alloy composition and resulting segregation issues during solidification impose practical limits on the melting rate and the maximum electrode or ingot diameters, which can be produced without gross irregularities. In order to reduce the incidence of melt-related irregularities, strict melt controls are imposed so as to monitor and control melt rate, heat input, melt temperature, electrode-to-crucible clearance, and other critical parameters. Inadequate control of these parameters can result in material with significant solidification-related irregularities which, in turn, can reduce yield and increase production costs. In melting procedures, such as vacuum induction melting and other processes, which require vessels with refractory linings, where one alloy is melted in the ceramic melt crucible, and then a second alloy of a different composition is to be subsequently melted in the same vessel, an intermediate "wash heat" may be required in order to minimize alloying

element contamination from one alloy to the next which may result from residual alloy material remaining on the crucible wall. This requirement adds to the overall cost of producing high-quality martensitic steel.

[0005] Irregularities may result from melting processes or as a result of subsequent forming operations. Melt-related irregularities include those related to segregation as well as those resulting from extrinsic contaminants such as air and crucible ceramics. Melting of martensitic steels is subject to significant solidification segregation that can result in the formation of irregularities such as freckles, eutectic nodules, white spots, and banding. Freckles are the result of alloying-element partitioning during solidification, and are most prevalent in those materials that are highly alloyed to achieve improved properties. White spots, likewise, are a result of alloying-element segregation, but can also be associated with extrinsic contamination from crucible ceramics or remnant slag inclusions (dirty white spots). Inclusions such as sulfides and carbosulfides may also form as a result of high sulfur contents in the melts. These melt-related irregularities can significantly degrade the fatigue resistance and/or toughness of the martensitic steel. Melt-related irregularities can also contribute to forging-related irregularities such as cracking. Some highly alloyed materials are also more difficult to form as a result of inheriting the coarse cast structure, which can lead to additional forging-related irregularities.

[0006] Some martensitic steels are produced using powder metallurgy processes to circumvent these segregation irregularity issues, particularly for large-diameter ingots, and to reduce the size of extrinsic contaminants resulting from the multiple melt process. The current powder metallurgy processes, however, require the martensitic steel composition to first be melted to produce alloy ingot, and then remelted and atomized to produce powder. These powder metallurgy processes add great expense and can still result in extrinsic contamination from crucible ceramics and slag. In addition, powder metallurgy processes are subject to concerns related to inert gas entrapment in powder particles during the atomization process, which can lead to residual porosity in the resulting billet or component. These irregularities can degrade

the fatigue and/or toughness properties of articles produced by the current powder metallurgy process.

[0007] The production of some desirable compositions of martensitic steels may be complicated by the differences in the thermophysical properties of the metals being combined to produce the alloy. The interactions and reactions due to these thermophysical properties of the metals may cause undesired results. To cite one example, the iron base metal is, in some cases, melted in a vacuum to ensure low contents of interstitial elements (e.g., oxygen, nitrogen, and sulfur) in the final alloys. In the work leading to the present invention, the inventors have realized that the necessity to melt under a vacuum makes it difficult to utilize some desirable alloying elements due to their relative vapor pressures in a vacuum environment. The difference in the vapor pressures is one of the thermophysical properties that must be considered in alloying such base metals. In other cases, the alloying elements may be thermophysically melt incompatible with the molten base metal because of other thermophysical characteristics such as miscibilities, melting points, densities, and chemical reactivities or may have limitations in alloy content due to solidification reactions which form undesirable phase morphologies. Some of the incompatibilities may be overcome with the use of expensive master alloys, but this approach is not applicable in other cases.

[0008] Thus, melting processes impose significant limitations on the resulting article. Incremental performance improvements resulting from processing modifications and incremental improvements in production cost reduction are still possible in a number of areas. However, the present inventors have recognized in the work leading to the present invention that in other instances the fabrication approach involving multiple melt steps imposes fundamental performance limitations that cannot be overcome at any reasonable cost. They have recognized a need for a departure from the conventional thinking in fabrication technology, which will overcome many of these fundamental limitations. The present invention fulfills this need, and further provides related advantages.

BRIEF SUMMARY OF THE INVENTION

[0009] The present invention provides a method for preparing a martensitic article made of an alloy of iron with a thermophysically melt-incompatible alloying element, in which the metal is never melted. Prior fabrication techniques require melting the metal at some point in the processing. The melting operation, which often involves multiple melting and solidification steps, is costly and imposes some fundamental limitations on the alloy content and hence the mechanical properties of the final martensitic-composition articles. The method circumvents problems, which cannot be avoided in melting practice or are circumvented only with great difficulty and expense. The present approach permits a uniform alloy to be prepared without subjecting the constituents to the circumstance, which leads to the incompatibility, specifically the melting process. Unintentional oxidation of the reactive metals and the alloying elements is also avoided. The present approach permits the preparation of articles with compositions that may not be otherwise readily prepared in commercial quantities. Master alloys are not used.

[0010] A martensitic-composition article of iron-base metal alloyed with an alloying element is prepared by mixing a chemically reducible nonmetallic base-metal precursor compound of the iron-base metal and a chemically reducible nonmetallic alloying-element precursor compound of an alloying element to form a compound mixture. The base metal, which is present in the alloy in an amount greater than any other element by weight, is iron. At least one alloying element is thermophysically melt incompatible with the base metal, but both thermophysically melt incompatible and thermophysically melt compatible alloying elements may be present. The method further includes chemically reducing the compound mixture to a metallic alloy, without melting the metallic alloy, and thereafter consolidating the metallic alloy to produce a consolidated metallic article, without melting the metallic alloy and without melting the consolidated metallic article, to produce a martensitic steel metallic article.

[0011] “Martensitic steel” as used herein is defined as having a composition of an iron-base alloy, wherein iron is present in an amount of at least about 50 percent by weight, which possesses a continuous body-centered cubic (BCC) or body-centered tetragonal (BCT) crystal structure matrix phase. At least about 75 percent by volume of the BCC or BCT matrix phase is present in an acicular phase morphology in the service condition, which develops as a result of a diffusionless phase transformation from the austenitic (face centered cubic, FCC) phase through non-equilibrium accelerated cooling (i.e., quenching). The martensite may or may not be tempered prior to service. The matrix may also contain additional phases in various phase morphologies in the as-quenched condition or after additional heat treatment or heat treatments. Phases such as austenite or ferrite, precipitates such as metal carbides and metal nitrides, and intermetallic compounds such as Ni_3Mo , FeTi , and Fe_2Mo may be present. The present approach first produces a “martensitic-composition” material which does not necessarily have the martensitic microstructure but which is capable to being heat treated to produce the martensitic microstructure, and this martensitic-composition material is thereafter heat treated to produce the martensitic steel. Typical steels falling within the definition used herein include martensitic stainless steels (e.g., M152 and 410), martensitic precipitation hardening stainless steels (e.g., 17-4PH), semiaustenitic precipitation hardening stainless steels (e.g., AM350 and AM355), maraging steels (e.g., Marage 250 and GE1014), and martensitic low alloy steels (e.g., 4340 and 52100).

[0012] The nonmetallic precursor compounds may be solid, liquid, or gaseous. The chemical reduction is preferably performed by solid-phase reduction, such as fused salt electrolysis of the precursor compounds in a finely divided solid form such as an oxide of the element; or by vapor-phase reduction, such as contacting vapor-phase halides of the base metal and the alloying element(s) with a liquid alkali metal or a liquid alkaline earth metal. The final article has more iron than any other element.

[0013] The mixture of the nonmetallic precursor compounds may be provided in any operable physical form. For example, the mixture may be furnished as a compressed mass of particles, powders, or pieces of the nonmetallic precursor compounds, which

typically has larger external dimensions than a desired final metallic article. The compressed mass may be formed by pressing and sintering. In another example, the mixture of the nonmetallic precursor compounds may be finely divided particulate or powder, and not compressed to a specific shape. In another example, the mixture may be a mixture of vapors of the precursor compounds.

[0014] In another embodiment, a method for preparing a martensitic iron-base article made of iron-base metal and alloyed with an alloying element comprises the steps of providing a chemically reducible nonmetallic base-metal precursor compound of the iron-base metal, and providing a chemically reducible nonmetallic alloying-element precursor compound of an alloying element that is thermophysically melt incompatible with the iron-base metal. The base-metal precursor compound and the alloying-element precursor compound are thereafter mixed together to form a compound mixture. The method further includes chemically reducing the compound mixture to produce a metallic alloy, without melting the metallic alloy, and thereafter consolidating the metallic alloy to produce a martensitic-composition consolidated metallic article, without melting the metallic alloy and without melting the martensitic-composition consolidated metallic article. Other compatible features described herein may be used with this embodiment.

[0015] The thermophysical melt incompatibility of the alloying element with the iron base metal may be any of several types, and some examples follow. Specific examples of thermophysical melt incompatibility for iron-base alloys are given. In the alloys, there are one or more thermophysically melt incompatible elements. Additionally, there may be, and usually are, one or more elements that are not thermophysically melt incompatible with the base metal. Some elements are not thermophysically melt incompatible when present in a “compatible” composition range (usually but not necessarily smaller amounts), but are thermophysically melt incompatible when present in an “incompatible” composition range (usually but not necessarily larger amounts). As used herein, such elements are considered to be thermophysically melt incompatible elements only when present in an amount within the incompatible composition range,

and are not considered to be thermophysically melt incompatible elements when present in an amount outside the incompatible composition range.

[0016] One such thermophysical melt incompatibility is in the vapor pressure, as where the alloying element has an evaporation rate of greater than about 10 times that of the base metal at a melt temperature, which is preferably a temperature just above (i.e., 50°C above) the liquidus temperature of the alloy. Examples of such alloying elements for iron-base alloys include barium, calcium, cadmium, cesium, lithium, magnesium, manganese, and zinc.

[0017] Another such thermophysical melt incompatibility occurs when the melting point of the alloying element is too high or too low to be compatible with that of the iron-base metal, as where the alloying element has a melting point different from (either greater than or less than) that of the iron-base metal of more than about 400°C (720°F). Examples of such alloying elements for iron-base alloys include aluminum, arsenic, cerium, copper, hafnium, lanthanum, manganese, molybdenum, tin, tantalum, tungsten, and zinc. Some of these elements may be furnished in master alloys whose melting points are closer to that of the iron-base metal, but the master alloys are often expensive.

[0018] Another such thermophysical melt incompatibility occurs when the density of the alloying element is so different from that of the iron base metal that the alloying element physically separates in the melt, as where the alloying element has a density difference with the base metal of greater than about 0.5 gram per cubic centimeter. Examples of such alloying elements for iron-base alloys include tantalum, tungsten, and niobium.

[0019] Another such thermophysical melt incompatibility occurs when the alloying element, or a chemical compound formed between the alloying element and the base metal, chemically reacts with the base metal in the liquid phase. Examples of such alloying elements for iron-base alloys include boron, gadolinium, hafnium, niobium, phosphorus, rhenium, silicon, tantalum, thorium, yttrium, zirconium, oxygen, nitrogen, and sulfur.

[0020] Another such thermophysical melt incompatibility is where the alloying element

exhibits a miscibility gap with the iron-base metal in the liquid phase. Examples of such alloying elements for iron-base alloys include silver, indium, magnesium, and oxygen.

[0021] Another such thermophysical melt incompatibility occurs due to elemental segregation during solidification, which causes an unacceptable distribution of the alloying element in the solidified ingot. The degree of segregation may be reduced in melted-and-cast product by lowering the melting power, reducing the ingot diameter, using long post-casting homogenization heat treatments, and the like, but these prior approaches increase cost and limit the type of product that may be produced. In the present process, this type of segregation is avoided because the alloy is never melted and solidified. Examples of such segregating alloying elements for iron-base alloys include arsenic, beryllium, antimony, scandium, and titanium.

[0022] Another thermophysical incompatibility is not strictly related to the nature of the base metal, but instead is related to the crucibles or environment in which the base metal is melted. Base metals may require the use of a particular crucible material or melting atmosphere, and some potential alloying elements may react with those crucible materials or melting atmospheres, and therefore not be candidates as alloying elements for that particular base metal. Examples of such incompatible alloying elements for iron-base alloys include hafnium, calcium, and cerium.

[0023] These and other types of thermophysical melt incompatibilities lead to difficulty or impossibility in forming acceptable martensitic alloys of these elements in a conventional melting practice. The present approach, in which the metals are not melted at all during production or processing, circumvents the thermophysical melt incompatibility to produce good quality, homogeneous alloys.

[0024] Some additional processing steps may be included in the present process. In some cases, it is preferred that the compound mixture be compacted, after the step of mixing and before the step of chemical reduction. The result is a compacted mass which, when chemically reduced, produces a compressed powder or a spongy metallic material. After the chemical reduction step, the metallic alloy is consolidated to

produce a consolidated metallic article, without melting the metallic alloy and without melting the consolidated metallic article. This consolidation may be performed with any physical form of the metallic alloy produced by the chemical reduction, but the approach is particularly advantageously applied to consolidating of the pre-compacted spongy material. Consolidation is preferably performed by hot pressing or hot isostatic pressing, or extrusion, but without melting in each case. Solid state diffusion of the alloying elements may also be used to achieve the consolidation.

[0025] Optionally, prior to the step of consolidating, a mixture of the metallic material and an “other additive constituent” may be produced to make the martensitic-alloy composition.

[0026] The consolidated metallic article may be used in the as-consolidated form. In appropriate circumstances, it may be formed to other shapes using known forming techniques such as rolling, forging, extrusion, and the like. It may also be post-processed by known techniques such as machining, heat treating, surface coating, and the like.

[0027] The present approach may be used to fabricate articles from the precursor compounds, entirely without melting. As a result, the characteristics of the alloying elements which lead to thermophysical melt incompatibility, such as excessive evaporation due to high vapor pressure, overly high or low melting point, overly high or low density, excessive chemical reactivity, strong segregation tendencies, and the presence of a miscibility gap, may still be present but do not normally lead to inhomogeneities or irregularities in the final metallic alloy. The present approach thus produces the desired alloy composition of good quality, but without interference from these thermophysical melt incompatibilities that otherwise would prevent the formation of an acceptable alloy.

[0028] The present approach differs from prior approaches in that the metal is not melted on a gross scale. Melting and its associated processing such as casting are expensive and also produce large-cast-grain-size microstructures and occasionally microstructures with local/long-range segregation such as eutectic nodules, white spots,

and freckles that either are unavoidable or can be altered only with additional expensive processing modifications. Undesirable second phases which precipitate in the melt or during solidification of liquid, which are stable and cannot be dissolved in subsequent solid state processing, are avoided. These second phases are a detriment to fatigue strength and/or toughness, and cannot be modified by subsequent processing. However, second phases may be introduced in a more-desirable dispersed form by the present meltless approach. The present approach reduces cost and avoids large grain sizes, detrimental coarse second phases, and irregularities associated with melting and casting, to improve the mechanical properties of the final metallic article. It also results in some cases in an improved ability to fabricate specialized shapes and forms more readily, and to inspect those articles more readily.

[0029] The preferred form of the present approach also has the advantage of being based in a powder-form precursor. Starting with a powder of the nonmetallic precursor compounds avoids a cast structure with its associated irregularities such as elemental segregation on a nonequilibrium microscopic and macroscopic level, a cast microstructure with a range of grain sizes and morphologies that must be homogenized in some manner for many applications, gas entrapment, and contamination. The present approach produces a uniform, fine-grained, homogeneous, pore-free, gas-pore-free, and low-contamination final product.

[0030] The fine-grain structure of the metallic material provides an excellent starting point for subsequent consolidation and metalworking procedures such as forging, hot isostatic pressing, rolling and extrusion. Conventional cast starting material must be worked to modify and reduce the scale of the microstructure, and such working is not necessary with the present approach.

[0031] Another important benefit of the present approach is improved inspectability as compared with cast-and-wrought product. The martensitic steel articles produced by the present approach are of a fine microstructural size and are free of microstructures discussed previously that inhibit inspectability. As a result, they exhibit a significantly reduced noise level during ultrasonic inspection, and permit inspection for smaller

irregularities. The reduction in size of irregularities that may be detected allows larger articles to be fabricated and inspected, thus permitting more economical fabrication procedures to be adopted, and/or the detection of smaller irregularities. By reducing the noise associated with the inspection procedure, larger diameter intermediate-stage articles may be processed and inspected. Processing steps and costs are reduced, and there is greater confidence in the inspected quality of the final product. The final article that contains fewer and smaller irregularities also results in improved mechanical properties.

[0032] The present approach also offers important benefits when used to make alloys of iron-base metal with conventional alloying elements that are not thermophysically incompatible with the base metal. Conventional melting-and-casting technology of commercial-scale heats of alloys, starting from ores of the metals, inevitably results in levels of impurity elements in the alloys. In some cases, the presence of the impurity elements produces highly undesirable effects on the properties of the alloys in service. In some cases the adverse effects of minor amounts of these elements has become evident only as the applications of the alloys becomes ever-more demanding. The present approach reduces, and in some cases eliminates entirely, the presence of such minor levels of impurity elements, due to the low-impurity nature of the starting materials and the low processing temperatures that are used, which limits the migration of impurity elements into the alloy. As a result, the strength, fatigue properties, and oxidation/sulfidization/corrosion resistance of the alloys are improved, as compared with the nominally same alloys produced by conventional techniques.

[0033] The present approach thus allows the production of new alloys that cannot be made with the present melting-and-casting technology because of thermophysical incompatibility. It also allows the production of existing alloys that can be made by melting-and-casting technology, but at lower cost and better quality than possible with the existing melting-and-casting technology, and with a more-desirable phase distribution.

[0034] The present approach is advantageously applied to make martensitic steel

articles. Contamination and other impurity elements that are almost unavoidable in conventional casting practice, and which may have major adverse effects on the properties of the material, may be eliminated with the present approach. The structure is more uniform and homogeneous than may be produced by conventional casting and working techniques. For the material produced by the present approach that replaces conventionally cast material, there is a reduced incidence of irregularities such as those produced by segregation and inclusions (e.g., white spots, freckles, eutectic nodules, and banding) during conventional casting operations, and those associated with remelted/recycled material. The cost is also reduced due to the elimination of processing steps associated with casting. The reduction in the cost of the final product achieved by the present approach also makes the martensitic steels more economical. Properties are also improved. Material made by the present approach that is a replacement for conventional wrought articles realizes these same benefits. Additionally, large-sized specialty articles, whose size is limited only by compaction capability, may be made while avoiding microsegregation and macrosegregation. Reduced thermomechanical work is required to produce fine microstructures, and there is reduced loading on the mechanical working equipment. More complex processing may be used, because of the initially fine microstructure.

[0035] Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention. The scope of the invention is not, however, limited to this preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036] Figure 1 is a perspective view of a metallic article prepared according to the present approach;

[0037] Figure 2 is a block flow diagram of an approach for practicing the invention; and

[0038] Figure 3 is a perspective view of a spongy mass of the metallic material.

DETAILED DESCRIPTION OF THE INVENTION

[0039] The present approach may be used to make a wide variety of metallic articles 20, such as a gas turbine shaft 22 of Figure 1. The shaft 22 is only one example of the types of articles 20 that may be fabricated by the present approach. Some other examples include other gas turbine parts such as stationary seals, bearing components, rings, cases, and frames, automobile parts, biomedical articles, and structural members such as airframe parts. There is no known limitation on the types of articles that may be made by this approach.

[0040] Figure 2 illustrates a preferred approach for an article of a base metal and a thermophysically melt-incompatible alloying element. The method includes providing a chemically reducible nonmetallic base-metal precursor compound, step 40, and providing a chemically reducible nonmetallic alloying-element precursor compound of an alloying element that is thermophysically melt incompatible with the base metal, step 42. "Nonmetallic precursor compounds" are nonmetallic compounds of the metals that eventually constitute the metallic article 20. Any operable nonmetallic precursor compounds may be used. Reducible oxides of the metals are the preferred nonmetallic precursor compounds in solid-phase reduction, but other types of nonmetallic compounds such as sulfides, carbides, halides, and nitrides are also operable. Reducible halides of the metals are the preferred nonmetallic precursor compounds in vapor-phase reduction. The preferred base-metal precursor compound is iron oxide for solid-phase reduction or iron chloride for vapor-phase reduction. The alloying element may be any element that is available in the chemically reducible form of the precursor compound. Mixtures of different types of precursor compounds may be used, as long as they are operable in the subsequent chemical reduction.

[0041] The martensitic-steel composition produced by the present approach is an iron-base alloy that may be heat treated to produce a martensitic-microstructure steel. The

base-metal compound is present in an amount such that, after the chemical reduction to be described subsequently, there is more of the iron base metal present in the metallic alloy than any other element. An "iron-base" alloy is defined as having more of the element iron than any other single element, and in many cases has more than 50 percent by weight of iron. The nonmetallic precursor compounds are selected to provide the necessary elements in the final metallic article, and are mixed together in the proper amounts to yield the necessary proportions of these metals in the final metallic article. For example, the final article may have a composition comparable to that of 17-4PH martensitic steel but with added cerium in an amount of more than about 1 weight percent. The cerium in this martensitic steel desirably combines with and getters oxygen and sulfur. If such a composition is melted, however, intermetallic compounds are formed in the melt to produce undesirable inclusions in the final material. The iron-cerium system has a low melting composition that results in an undesirable phase distribution upon solidification. There is also a concern with the presence of small particles of the furnace-refractory material. These potential problems are avoided by using the present non-melting approach. The cerium-modified 17-4 PH martensitic steel used for this example has a nominal major-element content of about 17 weight percent chromium, about 4 weight percent nickel, about 4 weight percent copper, about 0.3 percent niobium, about 1.5 percent cerium, balance iron, the nonmetallic precursor compounds would collectively contain these elements in the ratio of about 17 parts chromium to about 4 parts nickel to about 4 parts copper to about 0.3 parts niobium to about 1.5 parts cerium to about 73.2 parts iron, by weight. Other and minor alloying elements may also be provided in these and additional precursor compounds. The precursor compounds are furnished and mixed together in the correct proportions such that the ratio of the desired elements in the mixture of precursor compounds is that required to form the metallic martensitic steel in the final article. Nonmetallic precursor compounds that serve as a source of more than one of the metals in the final metallic article may also be used. Similar principles apply for other martensitic steels.

[0042] The nonmetallic precursor compounds are furnished in any operable physical

form. The nonmetallic precursor compounds used in solid-phase reduction are preferably initially in a finely divided form to ensure that they are chemically reacted in the subsequent step. Such finely divided forms include, for example, powder, granules, flakes, or pellets that are readily produced and are commercially available. The nonmetallic precursor compounds in this finely divided form may be processed through the remainder of the procedure described below. In a variation of this approach, the finely divided form of the nonmetallic precursor compounds may be compressed together, as for example by pressing and sintering, to produce a preform that is processed through the remainder of the procedure. In the latter case, the compressed mass of nonmetallic precursor compounds is larger in external dimensions than a desired final metallic article, as the external dimensions are reduced during the subsequent processing.

[0043] The present approach is utilized in conjunction with thermophysically melt incompatible alloying elements. "Thermophysical melt incompatibility" and related terms refer to the basic concept that any identified thermophysical property of an alloying element is sufficiently different from that of the base metal to cause detrimental effects in the melted final product. These detrimental effects include phenomena such as chemical inhomogeneity (detrimental micro-segregation, macro-segregation, and gross segregation from vaporization or immiscibility), inclusions of the alloying elements such as high-density inclusions, and the like. Thermophysical properties are intrinsic to the elements, and combinations of the elements, which form alloys, and are typically envisioned using equilibrium phase diagrams, vapor pressure versus temperature curves, curves of densities as a function of crystal structure and temperature, and similar approaches. Although alloy systems may only approach predicted equilibrium, these envisioning data provide information sufficient to recognize and predict the cause of the detrimental effects as thermophysical melt incompatibilities. However, the ability to recognize and predict these detrimental effects as a result of the thermophysical melt incompatibility does not eliminate them. The present approach provides a technique to minimize and desirably avoid the

detrimental effects by the elimination of melting in the preparation and processing of the alloy.

[0044] Thus, “thermophysical melt incompatible” and related terms mean that the alloying element or elements in the alloy to be produced do not form a well mixed, homogeneous alloy with the base metal in a production melting operation in a stable, controllable fashion. In some instances, a thermophysically melt incompatible alloying element cannot be readily incorporated into the alloy at any compositional level, and in other instances the alloying element can be incorporated at low levels but not at higher levels. For example, some elements do not behave in a thermophysically melt incompatible manner when introduced at low levels, and homogeneous alloys of such alloying additions may be prepared using a melting process. However, if there is an attempt to introduce greater levels of such elements, they tend to segregate strongly in the melt and thus behave in a thermophysically melt incompatible manner so that homogeneous alloys can only be prepared with great difficulty or not at all.

[0045] The thermophysical melt incompatibility of the alloying element with iron-base metal may be any of several types, and some examples follow.

[0046] One such thermophysical melt incompatibility is in the vapor pressure, as where the alloying element has an evaporation rate of greater than about 10 times that of the base metal at a melt temperature, which is preferably a temperature just above the liquidus temperature of the alloy. Examples of such alloying elements for iron-base alloys include barium, calcium, cadmium, cesium, lithium, magnesium, manganese, and zinc. Where the vapor pressure of the alloying element is too high, it will preferentially evaporate, as indicated by the evaporation rate values, when co-melted with iron-base metals under a vacuum in conventional melting practice. An alloy will be formed, but it is not stable during melting and continuously loses the alloying element so that the percentage of the alloying element in the final alloy is difficult to control. In the present approach, because there is no vacuum melting, the high melt vapor pressure of the alloying element is not a concern.

[0047] Another such thermophysical melt incompatibility occurs when the melting point

of the alloying element is too high or too low to be compatible with that of the iron-base metal, as where the alloying element has a melting point different from (either greater than or less than) that of the base metal of more than about 400°C (720°F). Examples of such alloying elements for iron-base alloys include aluminum, arsenic, cerium, copper, hafnium, lanthanum, manganese, molybdenum, tin, tantalum, tungsten, and zinc. Some of these elements may be furnished in master alloys whose melting points are closer to that of the iron-base metal, but the master alloys are often expensive. If the melting point of the alloying element is too high, it is difficult to melt and homogenize the alloying element into the melt in conventional vacuum melting practice. The segregation of such alloying elements may result in the formation of high-density inclusions containing that element. If the melting point of the alloying element is too low, it will likely have an excessively high vapor pressure at the temperature required to melt the base metal. In the present approach, because there is no vacuum melting, the overly high or low melting points are not a concern.

[0048] Another such thermophysical melt incompatibility occurs when the density of the alloying element is so different from that of the iron-base metal that the alloying element physically separates in the melt, as where the alloying element has a density difference with the base metal of greater than about 0.5 gram per cubic centimeter. Examples of such alloying elements for iron-base alloys include tantalum, tungsten, and niobium. In conventional melting practice, the overly high or low density leads to gravity-driven segregation of the alloying element. In the present approach, because there is no melting there can be no gravity-driven segregation.

[0049] Another such thermophysical melt incompatibility is where the alloying element, or a chemical compound formed between the alloying element and the base metal or another alloying element, chemically reacts with the base metal in the liquid phase. Examples of such alloying elements for iron-base alloys include boron, gadolinium, hafnium, niobium, phosphorus, rhenium, silicon, tantalum, thorium, yttrium, and zirconium. In conventional melting practice, the chemical reactivity of the alloying element with the base metal leads to the formation of intermetallic compounds including

the base metal and the alloying element, and/or other deleterious phases in the melt, which are retained after the melt is solidified. These phases often have adverse effects on the properties of the final alloy due to their large size and morphology. In the present approach, because the metals are not heated to the point where these reactions occur, the compounds are not formed or, if formed at lower temperatures, the morphologies cause minimal impact on the mechanical properties.

[0050] Another such thermophysical melt incompatibility is where the alloying element exhibits a miscibility gap with the base metal in the liquid phase. In conventional melting practice, a miscibility gap leads to a segregation of the melt into the compositions defined by the miscibility gap. The result is inhomogeneities in the melt, which are retained in the final solidified article. The inhomogeneities lead to variations in properties throughout the final article. In the present approach, because the elements are not melted, the miscibility gap is not a concern. Examples of such alloying elements, which exhibit a miscibility gap, for iron-base alloys include silver, indium, magnesium, and oxygen.

[0051] Another such thermophysical melt incompatibility occurs due to elemental segregation during solidification, which causes an unacceptable distribution of the alloying element in the solidified ingot. The degree of segregation may be reduced in melted-and-cast product by lowering the melting power, reducing the ingot diameter, using long post-casting homogenization heat treatments, and the like, but these prior approaches increase cost and limit the type of product that may be produced. In the present process, this type of segregation is avoided because the alloy is never melted and solidified. Examples of such segregating alloying elements for iron-base alloys include arsenic, beryllium, antimony, scandium, and titanium. The segregation of elements in conventional melting-and-casting practice results in adverse effects on mechanical properties as well as physical properties such as corrosion, oxidation, and sulfidization resistance.

[0052] Another thermophysical incompatibility is not strictly related to the nature of the base metal, but instead to the crucibles or environment in which the base metal is

melted. Base metals may require the use of a particular crucible material or melting atmosphere, and some potential alloying elements may react with those crucible materials or melting atmospheres, and therefore not be candidates as alloying elements for that particular base metal. Examples of such incompatible alloying elements for iron-base alloys include hafnium, calcium, and cerium.

[0053] These and other types of thermophysical melt incompatibilities lead to difficulty or impossibility in forming acceptable alloys of these elements in conventional production vacuum melting. Their adverse effects are avoided in the present meltless approach.

[0054] The base-metal compound and the alloying compound are mixed to form a uniform, homogeneous compound mixture, step 44. The mixing is performed by conventional procedures used to mix powders or form mixed oxides in other applications, for solid-phase reduction, or by the mixing of the vapors, for vapor-phase reduction.

[0055] Optionally, for solid-phase reduction of solid precursor compound powders the compound mixture is compacted to make a preform, step 46. This compaction is conducted by cold or hot pressing of the finely divided compounds, but not at such a high temperature that there is any melting of the compounds. The compacted shape may be sintered in the solid state to temporarily bind the particles together. The compacting desirably forms a shape similar to, but larger in dimensions than, the shape of the final article.

[0056] The mixture of nonmetallic precursor compounds is thereafter chemically reduced by any operable technique to produce a metallic material, without melting the metallic material, step 48. As used herein, “without melting”, “no melting”, and related concepts mean that the material is not macroscopically or grossly melted, so that it liquefies and loses its shape. There may be, for example, some minor amount of localized melting as low-melting-point elements melt and are diffusionally alloyed with the higher-melting-point elements that do not melt. Even in such cases, the gross shape of the material remains unchanged.

[0057] In one approach, termed solid-phase reduction because the nonmetallic precursor compounds are furnished as solids, the chemical reduction may be performed by fused salt electrolysis. Fused salt electrolysis is a known technique that is described, for example, in published patent application WO 99/64638, whose disclosure is incorporated herein by reference in its entirety. Briefly, in fused salt electrolysis the mixture of nonmetallic precursor compounds is immersed in an electrolysis cell in a fused salt electrolyte such as a chloride salt at a temperature below the melting temperature of the martensitic steel that forms from the nonmetallic precursor compounds. The mixture of nonmetallic precursor compounds is made the cathode of the electrolysis cell, with an inert anode. The elements combined with the metals in the nonmetallic precursor compounds, such as oxygen in the preferred case of oxide nonmetallic precursor compounds, are removed from the mixture by chemical reduction (i.e., the reverse of chemical oxidation). The reaction is performed at an elevated temperature. The cathodic potential is controlled to ensure that the reduction of the nonmetallic precursor compounds will occur, rather than other possible chemical reactions such as the decomposition of the molten salt. The electrolyte is a salt, preferably a salt that is more stable than the equivalent salt of the metals being refined and ideally very stable to remove the oxygen or other gas to a low level. The chlorides and mixtures of chlorides of barium, calcium, cesium, lithium, strontium, and yttrium are preferred as the molten salt. The chemical reduction may be carried to completion, so that the nonmetallic precursor compounds are completely reduced.

[0058] In another approach, termed vapor-phase reduction because the nonmetallic precursor compounds are furnished as vapors or gaseous phase, the chemical reduction may be performed by reducing mixtures of halides of the base metal and the alloying elements using a liquid alkali metal or a liquid alkaline earth metal. In one embodiment, a mixture of appropriate gases in the appropriate amounts is contacted to molten sodium, so that the metallic halides are reduced to the metallic form. The metallic martensitic steel is separated from the sodium. This reduction is performed at temperatures below the melting point of the metallic martensitic steel, so that the

martensitic steel is not melted. The approach is described more fully in U.S. Patents 5,779,761 and 5,958,106, whose disclosures are incorporated herein by reference in their entireties.

[0059] In this vapor-phase reduction approach, a nonmetallic modifying element or compound presented in a gaseous form may be mixed into the gaseous nonmetallic precursor compound prior to its reaction with the liquid alkali metal or the liquid alkaline earth metal. In one example, a carbon-containing gas may be mixed with the gaseous nonmetallic precursor compound(s) to increase the level of carbon in the martensitic steel. Similarly, elements such as sulfur, nitrogen, and boron may be added using appropriate gaseous compounds of these elements. Complex combinations of such gaseous elements may be provided and mixed together, such as gaseous compounds of nitrogen, sulfur, carbon, phosphorus, and/or boron, leading to precursor compound phase dissolution of such additive elements or to the formation of chemically more-complex second phases.

[0060] The physical form of the metallic material at the completion of step 48 depends upon the physical form of the mixture of nonmetallic precursor compounds at the beginning of step 48. If the mixture of nonmetallic precursor compounds is free-flowing, finely divided particles, powders, granules, pieces, or the like, the metallic material is also in the same form, except that it is smaller in size and typically somewhat porous. If the mixture of nonmetallic precursor compounds is a compressed mass of the finely divided particles, powders, granules, pieces, or the like, then the final physical form of the metallic material is typically in the form of a somewhat porous metallic sponge 60, as shown in Figure 3. The external dimensions of the metallic sponge are smaller than those of the compressed mass of the nonmetallic precursor compound due to the removal of the oxygen and/or other combined elements in the reduction step 48. If the mixture of nonmetallic precursor compounds is a vapor, then the final physical form of the metallic material is typically fine powder that may be further processed.

[0061] Some constituents, termed “other additive constituents”, may be difficult to introduce. For example, suitable nonmetallic precursor compounds of the constituents

may not be available, or the available nonmetallic precursor compounds of the other additive constituents may not be readily chemically reducible in a manner or at a temperature consistent with the chemical reduction of other nonmetallic precursor compounds. It may be necessary that such other additive constituents ultimately be present as elements in solid solution in the article, as compounds formed by reaction with other constituents of the article, or as already-reacted, substantially inert compounds dispersed through the article. These other additive constituents or precursors thereof may be introduced from the gas, liquid, or solid phase, as may be appropriate, using one of the four approaches subsequently described or other operable approaches.

[0062] In a first approach, the other additive constituents are furnished as elements or compounds and are mixed with the precursor compounds prior to or concurrently with the step of chemically reducing. The mixture of precursor compounds and other additive constituents is subjected to the chemical reduction treatment of step 48, but only the precursor compounds are actually reduced and the other additive constituents are not reduced.

[0063] In a second approach, the other additive constituents in the form of solid particles are furnished but are not subjected to the chemical reduction treatment. Instead, they are mixed with the initial metallic material that results from the chemical reduction step, but after the step of chemically reducing 48 is complete. This approach is particularly effective when the step of chemically reducing is performed on a flowing powder of the precursor compounds, but it also may be performed on a pre-compacted mass of the precursor compounds, resulting in a spongy mass of the initial metallic material. The other additive constituents are adhered to the surface of the powder or to the surface of, and into the porosity of, the spongy mass.

[0064] In a third approach, the precursor compounds are first produced as powder particles by compacting the precursor compounds of the metallic elements. The particles are then chemically reduced. The other additive constituent is thereafter produced at the surfaces of the particles from the gaseous phase. In one technique, a

gaseous precursor (e.g., methane) is flowed over the surface of the particles to deposit the element onto the surface from the gas.

[0065] A fourth approach is similar to the third approach, except that the other additive constituent is deposited from a liquid rather than from a gas. The precursor is first produced as powder particles by compacting the precursor compounds of the metallic elements. The particles are then chemically reduced. The other additive constituent is thereafter produced at the surfaces of the particles by deposition from the liquid. In one technique, the particulate is dipped into a liquid solution of a precursor compound of the other additive constituent to coat the surfaces of the particles. The precursor compound of the other additive constituent is second chemically reacted to leave the other additive constituent at the surfaces of the particles. In an example, lanthanum may be introduced into the material by coating the surfaces of the reduced particles with lanthanum chloride. The coated particles are thereafter heated and/or exposed to vacuum to drive off the chlorine, leaving lanthanum at the surfaces of the particles.

[0066] Whatever the reduction technique used in step 42 and however the other additive constituent is introduced, the result is a mixture that comprises the desired composition.

[0067] The chemical composition of the metallic alloy is determined by the types and amounts of the metals in the mixture of nonmetallic precursor compounds furnished in steps 40 and 42. The relative proportions of the metallic elements are determined by their respective ratios in the mixture of step 44 (not by the respective ratios of the compounds, but the respective ratios of the metallic element). Here, the metallic alloy has more iron than any other element, producing an iron-base metallic alloy.

[0068] At this stage, the metallic martensitic-composition material is in a form that is not structurally useful for most applications. Accordingly, the metallic martensitic steel is thereafter consolidated to produce a consolidated metallic article, without melting the metallic martensitic steel and without melting the consolidated metallic article, step 50. The consolidation removes porosity from the metallic martensitic steel, desirably increasing its relative density to or near 100 percent. Any operable type of consolidation may be used. Preferably, the consolidation 50 is performed by hot

isostatic pressing the metallic martensitic steel under appropriate conditions of temperature and pressure, but at a temperature less than the melting points of the metallic martensitic steel and the consolidated metallic article (which melting points are typically the same or very close together). Pressing and solid-state sintering or extrusion of a canned material may also be used, particularly where the martensitic steel is in the form of a powder. The consolidation reduces the external dimensions of the mass of metallic martensitic steel, but such reduction in dimensions is predictable with experience for particular compositions. The consolidation processing 50 may also be used to achieve further alloying of the metallic article with alloying elements such as nitrogen and carbon.

[0069] The consolidated metallic article, such as that shown in Figure 1, may be used in its as-consolidated form. Instead, in appropriate cases the consolidated metallic article may optionally be post processed, step 52. The post processing may include forming by any operable metallic forming process, as by forging, extrusion, rolling, and the like. Some metallic compositions are amenable to such forming operations, and others are not. The martensitic steel article consolidated by the present approach will be much more amenable to forming operations than its equivalent conventionally prepared (i.e., cast or cast-and-wrought) composition due to its finer grain size and potential for superplastic forming. The consolidated metallic article may also or instead be optionally post-processed by other conventional metal processing techniques in step 52. Such post-processing may include, for example, heat treating, surface coating, machining, and the like. The post-processing, when performed, may include one or more of such individual post-processing operations.

[0070] One important post-processing step 52 is heat treating to produce an acicular phase morphology characteristic of a martensitic microstructure. The material produced to this point in the processing is of a composition that forms a martensitic microstructure, but it will not generally have a martensitic microstructure until properly heat treated (although there may be martensite coincidentally present). Such heat treatments are known in the art for the various compositions produced by other

techniques, but generally involve heating above a required temperature, known for each composition, and then a relatively rapid cooling (i.e., quenching) to produce the martensitic structure. The same heat treatment procedures used for martensitic-composition steels produced by other techniques are used with the martensitic-composition steels produced by the present meltless approach. The heat treating may be performed at this point prior to other post-processing, after other post-processing, or between individual post-processing procedures.

[0071] The martensitic steel is never heated above its melting point. Additionally, it may be maintained below specific temperatures that are themselves below the melting point, such as various precipitate (e.g., non-metallic particles such as carbides, or intermetallic particles) solvus temperatures. Such temperatures are known in the art for the specific compositions.

[0072] In other cases, it is desirable to heat the martensitic steel above a particular solvus temperature in order to achieve a specific type of microstructure. Such temperatures are known in the art for the specific compositions.

[0073] The microstructural type, morphology, and scale of the article is determined by the starting materials and the processing. The grains of the articles produced by the present approach generally correspond to the morphology and size of the powder particles of the starting materials, when the solid-phase reduction technique is used. In the present approach, the metal is never melted and cooled from the melt, so that the coarse grain structure associated with the solidified structure never occurs. In conventional melt-based practice, subsequent metalworking processes are designed to break up and reduce the coarse grain structure associated with solidification. Such processing is not required in the present approach.

[0074] The present approach processes the mixture of nonmetallic precursor compounds to a finished metallic form without the metal of the finished metallic form ever being heated above its melting point. Consequently, the process avoids the costs associated with melting operations, such as controlled-atmosphere or vacuum furnace costs. The microstructures associated with melting, typically large-grained structures, casting

irregularities, and segregation-related irregularities (e.g., freckles, white spots, and eutectic nodules), are not found. Without such irregularities, the reliability of the articles is improved. The greater confidence in the irregularity-free state of the article, achieved with the better inspectability discussed above, also leads to a reduction in the extra material that must otherwise be present. Mechanical properties such as static strength, fatigue strength, and toughness may be improved, potentially allowing the articles to be lighter in weight. Inspectability is improved, and the product has reduced cost, irregularities, and porosity, as compared with the product of other powder metallurgy processing.

[0075] Although a particular embodiment of the invention has been described in detail for purposes of illustration, various modifications and enhancements may be made without departing from the spirit and scope of the invention. Accordingly, the invention is not to be limited except as by the appended claims.